

PATENT ABSTRACTS OF JAPAN

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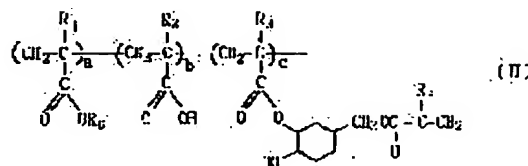
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(54) ALKALI-DEVELOPABLE PHOTODEVELOPING RESIN COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an alkali-developable photodeveloping resin composition giving a dry coating film having satisfactorily improved tackiness after coating and drying on a substrate.

SOLUTION: The tack-free alkali-developable photodeveloping resin composition is obtained by blending the following components (A)-(D) as essential components with ultrafine particulate silica powder as a filler; (A) a modified copolymer represented by formula (II) (where R₁-R₄ may be the same or different and are each H or methyl; R₅ is a 1-5C alkyl having a straight chain or side chain structure; and a, b and c are each a degree of polymerization) and having carboxyl and acrylic groups in side chains, (B) photopolymerizable vinyl monomers which are di(meth)acrylates of ≥7C alkane diols having a linear and/or cyclic structure, (C) a photopolymerization initiator, (D) a solvent.



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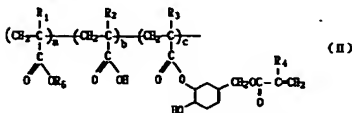
CLAIMS

[Claim(s)]

[Claim 1] The alkali development mold photo-setting resin constituent of the tack free nature which uses following (A), (B), (C), and (D) as an indispensable component, and is characterized by blending ultrafine particle-like silica powder as a bulking agent.

(A) General formula (II)

[Formula 1]



the inside of [type, and R1, R2, R3 and R4 are the same — or you may differ, a hydrogen atom or a methyl group is expressed, and R5 expresses the straight chain of carbon numbers 1-5, or the alkyl group of side-chain structure. a, b, and c express polymerization degree.]

The denaturation copolymer which comes out and has a carboxyl group and an acrylic radical in the side chain shown.

(B) The photopolymerization nature vinyl monomer which is di(meth)acrylate of the alkane diols which have the with a carbon numbers of seven or more shape of a chain, and /cyclic structure.

(C) Photopolymerization initiator.

(D) Organic solvent.

(c) Organic solvent.

[Claim 2] The alkali development mold photo-setting resin constituent of the tack free nature according to claim 1 characterized by being 0.2 ~ 2 weight section to this constituent 100 weight section in which the pitch diameter of the primary particle of ultrafine particle-like silica powder is in the range of 5~20nm (nm), and the loadings do not contain silica powder.

[Claim 3] The alkali development mold photo-setting resin constituent of tack free nature according to claim 1 with which a photopolymerization nature vinyl monomer is characterized by being one sort or two sorts or more of mixture of 1, 8-octane JIORUJI (meta) acrylate, 1, 9-nonane JIORUJI (meta) acrylate, 1, 10-decane JIORUJI (meta) acrylate, cyclohexane JIMETANORUJI (meta) acrylate, and dimethylol tricyclo DEKANJI (meta) acrylate.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the still more detailed etching resist for printed-circuit boards about an alkali development mold photo-setting resin constituent, and the other various etching resist for metalworking.

[0002]

[Description of the Prior Art] From the former, the photo-setting resin constituent which consists of giant-molecule binder resin, a photopolymerization nature vinyl monomer, and a photopolymerization initiator has been used for the various etching resist for metalworking including a printed-circuit board. With development of various lithographic plates and the electronics field, in order to obtain a detailed pattern, high resolution and the photoresist constituent of high sensitivity are proposed variously in recent years. Moreover, various constituents which can carry out a development in a dilute-alkali water solution for an improvement of workability and work environment are also proposed. However, the present condition is that the property (tack nature) in which the dry paint film after the sensitization liquid these-proposed applying sensitization liquid to a substrate in respect of practical use and drying is sticky is not fully improved. Therefore, in the subsequent routing, in the case of the handling of a spreading substrate, adhesion and exfoliation of a hardening paint film often occur, and have the problem that the yield and working efficiency worsen.

[0003]

[Problem(s) to be Solved by the Invention] Like the above-mentioned, said resist is still inadequate from a practical use side about the tack free engine performance, and the problem is not solved. By adhering to a paint film with the heat which the mask pattern to which it is stuck by the paint film especially at the time of exposure generates from an aligner, when a paint film adheres to other substrates during handling of the problem that working capacity worsens, and a spreading substrate, damage on a paint film breaks out, or problems, such as causing trouble, are in the activity of degree process. In said etching resist, the further improvement of the tack free nature of a dry paint film has been a technical problem from this situation.

[0004]

[Means for Solving the Problem] As a result of examining wholeheartedly the means for giving tack free nature to an alkali development mold photo-setting resin constituent that said technical problem should be solved, by making said constituent contain ultrafine particle silica powder as a bulking agent, this invention persons find out that the tack free nature of a dry paint film is markedly alike, and improves, and came to make this invention.

[0005] The alkali development mold photo-setting resin constituent of the tack free nature of this invention is a constituent which uses following (A), (B), (C), and (D) as an indispensable component, and is characterized by blending ultrafine particle-like silica powder as a bulking agent.

(A) General formula (I)

[Formula 2]

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2006/12/01

by this invention, it is desirable that it is in the range of 50 ~ 150 mgKOH/g. When the acid number becomes 50 or less mgKOH/g, removal of a non-hardening resin constituent is difficult at the time of the development by the dilute-alkali water solution. On the other hand, if the acid number will be 150 or more mgKOH/g, an image may flow at the time of the development by the dilute-alkali water solution, or the moisture resistance of a hardening coat may worsen. Moreover, the weight average molecular weight (Mw) of a denaturation copolymer (A) has the desirable range of 5,000~20,000. There is a problem that the moisture resistance of the paint film after exposure is bad, and the tack free engine performance is inferior in the weight average molecular weight of a denaturation copolymer (A) being 5,000 or less, and resolution is [****] arises and [] greatly inferior at the time of development. On the other hand, if weight average molecular weight exceeds 20,000, problems, like the development nature by the dilute-alkali water solution getting remarkably bad and storage stability are inferior will arise.

[0010] Furthermore — although there is no limit especially in the ratio of an epoxy group content unsaturated compound and a carboxyl group content acrylic copolymer on the occasion of the ring breakage addition reaction mentioned above — per 1kg of resin after a ring breakage addition reaction — a double bond — usually — 1.3~3.5 mols, i.e., the double bond equivalent 1,000 ~ 288 g/mol partial saturation radical, — it is 1.5~3.5 mols (the double bond equivalent 687 ~ 333 g/mol) preferably. When fewer than 1.0 mols, enough photo-curing objects may not be obtained for the denaturation copolymer (A) concerned. Moreover, in [] than 3.5 mols [] more, there are problems — it is hard to acquire sufficient storage stability.

[0011] As a product applicable to the denaturation copolymer (A) concerned, the commercial item of the "SAIKUROMAP" by Daicel Chemical Industries, Ltd. is carried out, for example, and it can be used in this invention. Four brands shown in the following table are marketed by said SAIKUROMAP, and any product of a brand can be used for it in this invention. Each of these brands makes methyl acrylate (3, 4-epoxycyclohexyl) add to a methacrylic-acid-methyl-methacrylate copolymer (I).

[Table 1]

一 般 性 質 :

品 名	ACA200	ACA200B	ACA250	ACA210F
外 観	無色液体	無色液体	無色液体	無色液体
粘 度 ^a	879c	807c	899c	886c/776
固 形 分 (wt%)	45~50	45~50	45~50	46~52
密 度 (g/cm ³ 25℃)	1.0000	0.9999	1.0000	1.0000
重量平均分子量	79000	12000	8000	80000
重量平均分子量 (GPC 法)	110~120	110~120	70~80	120~130
重量平均分子量 (GPC 法)	15000	10000	9000	25000
二 重 結 合 率 (計算値)	1.000	1.000	1.000	2.000
二 重 結 合 率 (計算値)	4.50	4.50	3.00	4.50
融 点 (℃)	1.37	1.37	1.36	1.40

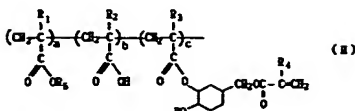
^a MFDG: ジブチルベンジレート/メタクリル酸 (濃度 10.7. 2℃)

MMPG: プロピレングリコールモノアクリレート (濃度 13.1℃)

PFG: プロピレングリコールモノアクリレート (濃度 14.9. 8℃)

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2006/12/01



the inside of (type, and R1, R2, R3 and R4 are the same — or you may differ, a hydrogen atom or a methyl group is expressed, and R5 expresses the straight chain of carbon numbers 1~5, or the alkyl group of side-chain structure. a, b, and c express polymerization degree.] The denaturation copolymer which comes out and has a carboxyl group and an acrylic radical in the side chain shown.

(B) The photopolymerization nature vinyl monomer which is di(meth)acrylate of the alkane diols which have the with a carbon numbers of seven or more shape of a chain, and /cyclic structure.

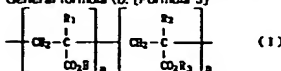
(C) Photopolymerization initiator.

(D) Organic solvent.

[0006]

[Embodiment of the Invention] The detail of this invention is explained below. The component (A) used by this invention is a denaturation copolymer which has a carboxyl group and an acrylic radical in the side chain which is made to carry out the ring breakage addition reaction of the acyclic epoxy group content unsaturated compound (II) which has the vinyl group and epoxy group more than a piece in a monad to the copolymer (I) containing the segment which has a carboxyl group, and is obtained. As a copolymer (I) containing the segment which has said carboxyl group, the copolymer (I) shown by the following general formula (I) can be illustrated.

General formula (I) [Formula 3]



the inside of (type, R1, and R2 are the same — or you may differ, a hydrogen atom or a methyl group is expressed, and R3 expresses the straight chain of carbon numbers 1~5, or the alkyl group of side-chain structure. Moreover, m and n express polymerization degree and are m/n=0.5~2.4 (mole ratio).]

[0007] Specifically as a copolymer (I), a methacrylic-acid-acrylic ester copolymer, a methacrylic-acid-methacrylic ester copolymer, an acrylic-acid-acrylic ester copolymer, an acrylic-acid-methacrylic ester copolymer, etc. are mentioned. Furthermore, specifically, a methacrylic-acid-butyl acrylate copolymer, a methacrylic-acid-methyl-methacrylate copolymer, an acrylic-acid-butyl acrylate copolymer, an acrylic-acid-methyl-methacrylate copolymer, etc. are mentioned. Moreover, as an acyclic epoxy group content unsaturated compound (II) used by this invention, methyl methacrylate (3, 4-epoxycyclohexyl) or (3, 4-epoxycyclohexyl) methyl acrylate is desirable.

[0008] Therefore, the denaturation copolymer shown by said general formula (II) which is made to carry out the ring breakage addition reaction of the epoxy group content unsaturated compound (II) chosen from methyl methacrylate (3, 4-epoxycyclohexyl) or (3, 4-epoxycyclohexyl) methyl acrylate as the copolymer (I) which contains in a side chain the segment which has a carboxyl group as a denaturation copolymer (A) which has a carboxyl group and an acrylic radical, and is obtained is desirable. It is said that it is improved compared with the case where the tack free nature of a dry paint film uses conventional resin as the description of such a denaturation copolymer (A) is indicated by JP.1-29820A, JP.8-41150A, JP.8-259624A, JP.8-26221A, JP.9-278842A, JP.9-278869A, JP.10-7755A, JP.10-10726A, JP.10-17644A, etc.

[0009] As for the acid number (K-JIS 1557 conformity) of the denaturation copolymer (A) used

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[0013] Although the photo-setting resin constituent of this invention can blend a photopolymerization nature polyfunctional vinyl monomer, it is characterized by using the polymerization nature vinyl monomer which consists of JI (meta) acrylic ester of the chain-like type of seven or more carbon numbers, and/or **** type alkane diols as a photopolymerization nature vinyl monomer of the component (B) used by this invention. As a suitable photopolymerization nature vinyl monomer (B) used by this invention, 1, 8-octane JIORUJI (meta) acrylate, 1, 9-nonane JIORUJI (meta) acrylate, 1, 10-decane JIORUJI (meta) acrylate, cyclohexane JIMETANORUJI (meta) acrylate, dimethylol tricyclo DEKANUJI (meta) acrylate, hydrogenation bisphenol F di(meth)acrylate, hydrogenation BIFENORUJI (meta) acrylate, etc. can specifically be illustrated. These can be used as one sort or two sorts or more of mixture, when 1, 9-nonane diol diacrylate, 1, 10-Decane diol diacrylate, and cyclohexane dimethanol diacrylate are used especially, while the outstanding sensibility and resolution are acquired, the tack free nature of a dry paint film is markedly alike, and improves.

[0014] 1 ~ 25 weight section is suitable for the loadings of the photopolymerization nature vinyl monomer (B) in the constituent of this invention to the denaturation (copolymer A) 100 weight section. If the loadings of a photopolymerization nature vinyl monomer exceed 25 weight sections, the problem that the tack free nature of a dry paint film and the development nature by the alkali water solution are inferior will arise. On the other hand, if it becomes below 1 weight section, sensibility and resolving power will be inferior and it will be set to the level which does not bear practical use. Furthermore, indeed, since sensibility becomes high, according to various dry films resist, sensibility accommodation is possible for it, if the addition of a photopolymerization nature vinyl monomer (B) increases.

[0015] The constituent concerned containing a denaturation copolymer (A) turns into a photo-setting resin constituent of this invention by blending a photopolymerization initiator. As a photopolymerization initiator (C), there is especially no limit and it can use various things, such as a halo methyl oxazole system compound, a halo methyl-s-triazine compound, onium salt, benzoin ether, benzophenones, xanthones, an acetophenone derivative, and azide. In combination with a denaturation copolymer (A) component, the constituent of this invention in respect of image formation nature As a photopolymerization initiator, the 4-dimethylamino ethyl benzoate (Nippon Kayaku Co., Ltd. kaysa cure EPA Three kinds of 1-butanones [IRUGA cure 369 Made from tba specialty chemical]) are mixed. 2 and 4-diethyl thioxan tol (Nippon Kayaku Co., Ltd. kaysa cure DETX) and 2-benzyl-2-N, and N-dimethylamino-1-(4-morpholino phenyl) — It is good to use, as a sensitizer — 2-nitro fluorene, and 4-7-trinitro full — me — non, bends anthrone, PKURAMIDO, 1, 2-Anthraquinone, 1, and 1-chloro-6-hydroxy bends anthrone, phenan surthone, quinone, 4-(4-butoxy phenyl)-2, and 6-diphenyl thio pyrylium PAKURETO etc. can be illustrated.

[0016] Furthermore, to the photo-setting resin constituent of this invention, it can add with extent which does not check hardening according the thermal polymerization inhibitor commonly used in this kind of field as other additives, a leveling agent, a silicone system or a fluorine system deforming agent, an antioxidant, a filler, a color pigment, a coloring color, etc. to an activity energy line.

[0017] Although an organic solvent (D) is used for preparation of the constituent concerned in this invention, as an organic solvent, there is especially no limit, various solvents, such as ester, alcohols, ether, and ketones, can be used, it is independent or mixing and using is possible. A solvent is suitably chosen by the property of various coaters. As a solvent, alcohols, such as a methanol, ethanol, and 2-propanol, Ketones, such as an acetone, a methyl ethyl ketone, and methyl isobutyl ketone Ether, such as diethylether, dibutyl ether, and dioxane, Ethyl acetate, isobutyl acetate, ethylene glycol mono-acetate, Ester, such as propylene glycol mono-acetate and dipropylene glycol mono-acetate Ethylene glycol monoalkyl ether and diethylene glycol monoalkyl ether Propylene glycol monoalkyl ether and dipropylene glycol monoalkyl ether Ethylene glycol dialkyl ether, propylene glycol dialkyl ether, Diethylene glycol wood ether, the diethylene glycol dialkyl ether of diethylene glycol diethylether, Dipropylene glycol dialkyl ether, such as dipropylene glycol wood ether and dipropylene glycol diethylether, Ethylene glycol monoalkyl ether acetate, propylene glycol monoalkyl ether acetate, diethylene glycol monoalkyl ether

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monoalkyl ether acetate, and dipropylene glycol monoalkyl ether acetate are mentioned.

[0018] In this invention, as ultrafine particle silica powder used as a bulking agent, the pitch diameter of a primary particle is 5–30nm (nano meter), and a 5–20nm thing is used suitably. Furthermore, on this particle front face, the silica of the hydrophilic property which has a silanol group (–SiOH) has the good dispersibility to a medium, and is used suitably. Such ultrafine particle silica powder is marketed by the trade name of "AEROSIL (Aerosil)" from Japanese Aerosil, Inc. As hydrophilic grade, although 50, 90G, 130,200,200V, 200CF, 200FAD, 300,300CF, 380, etc. are marketed, standard type #200 are usually used in this. The main physicochemical data of above-mentioned #200 are as follows.

– Specific surface area by the BET adsorption method : PH value in 200m2 / g, 4% water dispersion : Pitch diameter of the 4.0–4.5, 1st particles : About 12nm and apparent specific gravity : 50 g/L–SiO2 Content : > 99.9% [0019] moreover, the ultrafine particle silica powder in this invention — the constituent 100 weight section — receiving — 1 – 10 weight section — it is 1 – 5 weight section preferably. If the above-mentioned loadings exceed 10 weight sections, a thixotropy will appear notably at the time of constituent preparation, and mixed actuation will become difficult as a matter of fact. On the other hand, if it becomes below 1 weight section, the problem that the tack free nature of a dry paint film is inferior will arise. Moreover, even if it blends ultrafine particle silica powder in this way, the sensitization property when sensitization properties, such as sensibility and resolution, not being spoiled and not adding this is maintained. Furthermore, it is obtained, a paint film shows good resistance also to etching reagents, such as a ferric chloride water solution, and the evil by blending ultrafine particle silica powder is not seen.

[0020] The approach of forming a coat using the constituent of this invention is enforced as follows. A natural roll coater, a reverse roll coater, a gravure roll coater, a screen printer, a curtain coating machine, an air spray, a bar coating machine, a knife coating machine, a spin coater, the brush, an immersion (DIP) coater, etc. are used for a substrate or metal vacuum evaporation plates, such as glass, plastics, and a metal (zinc, iron, copper, aluminum, or these alloys), and the constituent concerned is applied to them. Surface treatment of said substrate may be carried out with heat-treatment, surface polish, etching, or drugs, and it may improve a property. Moreover, in order to improve the adhesion between this invention constituent and a substrate, an adhesion accelerator may be included in said constituent, for example, a silane coupling agent may be blended.

[0021] Although thickness changes with applicable fields, it is good to usually consider as the range of 1–70 micrometers. Subsequently, the obtained spreading object is dried in a room temperature or an air heater, and the application film is made to form. Whenever [stoving temperature] can be heated to the temperature from which degradation of said constituent and a substrate does not arise, for example, 150 degrees C. It exposes by irradiating an activity energy line through a negative mask at the obtained application film using a high pressure mercury vapor lamp, an ultrahigh pressure mercury lamp, a xenon lamp, a metal halide lamp, etc. Subsequently, the approach of developing negatives by the spray gun, dip coating, or the pad method, and forming a 1–70-micrometer resist pattern with a dry paint film is adopted. Subsequently, a development is carried out with an alkali developer.

[0022] A dilute-alkali water solution is used for the development of the application film formed with the photo-setting resin constituent of this invention. As an alkali component of said dilute-alkali water solution Specifically The hydroxide of alkali metal, such as a lithium, sodium, and a potassium, inorganic bases, such as a carbonate, a bicarbonate, and phosphate, a pyrophosphate, benzylamine. Primary amine, such as a butylamine, dimethylamine, dibenzylamine. Secondary amine, such as diethanolamine, a trimethylamine, triethylamine, Tertiary amine, such as triethanolamine, a morpholine, a piperazine, Polyamine, such as annular amines, such as a pyridine, ethylenediamine, and a hexamethylenediamine. Tetraethylammonium hydroxide, trimethyl benzyl ammonium hydroxide, Ammonium hydroxide, such as trimethyl phenyl benzyl ammonium hydroxide and a choline The mixed liquor of these alkali component and the buffer solution is mentioned to sulfonium hydroxide, such as trimethylsulfonium hydroxide, diethylmethysulfonium hydroxide, and dimethylbenzylsulfonium hydroxide, and a list. One sort or two sorts or more of

such mixture is used.

[0023] The amount of the alkali component used of the dilute-alkali water solution for development is not limited that what is necessary is [especially] just extent used as a dilute alkali. For example, 0.5 – 5% of the weight of a sodium-carbonate water solution is usually used as a dilute-alkali water solution. Like the above, as for the resist pattern paint film which carried out the development, postbake of 10 minutes – about 3 hours is further given at the temperature of 100–200 degrees C if needed. Polymerization hardening of a paint film can be advanced further by this, and thermal resistance, etching-proof nature, adhesion, and tack free nature can be raised. Although the photo-setting resin constituent of this invention is used for a photoresist, etching resist, a solder resist, a dry film resist, a lithographic plate, etc., when using it as etching resist, it processes the resist pattern formed on the substrate as mentioned above with an etching reagent, and carries out imprint formation of the pattern of the request to a substrate. Especially as an etching reagent, although not limited, water solutions, such as a ferric chloride and a cupric chloride, are usually used. Subsequently exfoliation processing of a paint film is performed after etching processing termination using an alkali water solution. Although especially exfoliation processing is not limited, if a caustic-alkali-of-sodium water solution is heated at 60 degrees C or more 5 to 10% and it processes, it can exfoliate easily.

[0024]

[Example] Hereafter, although an example explains this invention concretely, this invention is not limited to these examples at all.

[0025] As a preparation (preparation of undiluted solution) denaturation copolymer (A) of an example 1 (1) constituent SAIKUROMAP by Daicel Chemical Industries, Ltd. Brand ACA-200M as 500g and a photopolymerization nature vinyl monomer (B) As 1 and 9-nonane diol acrylate (1, 9-ND-A) 24g and a photopolymerization initiator (C) Kaya cure EPA 12g, kays cure DETX 12g and IRUGA cure 369 As 12g mixture and a solvent (D), propylene-glycol-monomethyl-ether (PGM) 500g was added to the flask with a stirrer, and it stirred until it dissolved completely. Subsequently, it is an aperture about the obtained solution. Precision filtration was performed through the 0.5-micrometer filter, and the constituent undiluted solution was prepared.

* SAIKUROMAP ACA-200M : [Daicel Chemical Industries, Ltd. make] Acid number 118 mg KOH/g Double bond equivalence 450 g/mol Weight average molecular weight Mw 13000 Kays cure EPA : * The Nippon Kayaku Co., Ltd. make 4-dimethyl ethyl benzoate * kays cure DETX : [Nippon Kayaku Co., Ltd. make] 2, 4-diethyl xanthone * kays cure 369 : [The product made from the special tee KEMIKARUZU] 2-benzyl-2-N and N-dimethylamino-1- (4-morpholino phenyl) – 1-butanone [0026] <Distribution of ultrafine particle silica powder>, next the above-mentioned undiluted solution 500g and AEROSIL200 made from Japanese Aerosil 25g was bet on the sand mill for 1 hour, and silica powder was fully distributed.

The (last preparation of a constituent), next the above-mentioned undiluted solution 300g and the 75g of the above-mentioned dispersion liquid were measured in the flask with a stirrer, and stirring mixing was carried out for picking about 1 hour. In this case, the loadings of AEROSIL200 were the 0.98 weight section to said sensitization liquid undiluted solution 100 weight section.

[0027] (2) The cleaning 42 alloy (42 nickel-Fe alloy) plate of a substrate was immersed in Jusco clean No.5 made from Japanese Surface Preparation 60-degree C water solution for 2 minutes, and alkali degreasing was performed. Subsequently, rinsing / desiccation processing was carried out. The following evaluation trials were presented with this.

(3) The sensitization liquid prepared by spreading and the prebake above (1) of sensitization liquid was applied so that a whirler coater might be used for 42 alloy substrate of the above (2) and resist thickness might be set to about 10 micrometers. After spreading, in order to dry a spreading plate further, rotation was continued for 3 minutes. Subsequently, the hot blast by which the temperature control was carried out to 80 degrees C – constant temperature – said spreading plate was put in for 10 minutes into the drier, and prebake processing was performed.

[0028] (4) The spreading side of the substrate which carried out exposure prebake processing — a resolving chart (test pattern) and the product made from KODAKKU — it exposed for 2 minutes in the distance of 1m using 1Kw ultrahigh pressure mercury lamp, carrying out vacuum adhesion of step tablet No.2.

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Illuminance 320–390nm 1.77 mw/cm2 330–490nm It was usually immersed for 60 – 80 seconds into 25-degree C 0.5% sodium-carbonate water solution, and bat development of the substrate which the 6.8 mw/cm2(5) development above (4) exposed was carried out. Then, rinsing processing was carried out.

[0029] (6) the hot blast by which the temperature control was carried out to postbake 150 degree C – constant temperature – the substrate with which the pattern of the above (5) was formed into the drier was put in for 10 minutes, and postbake processing was performed.

(7) Spray etching was performed for the substrate which carried out postbake processing by the etching test above (6) for 5 minutes at 50 degrees C using the 45-degreeBe' ferric-chloride water solution.

[0030] The trial evaluation criteria carried out at each above-mentioned process are as follows. The obtained evaluation result was shown in Table 1.

The sensitization liquid with which uses a HOERA coater and a trial is presented was applied on the glass substrate of (parameter and its measuring method) (1) tuck engine-performance 10x10cm size. Subsequently, prebake of the glass substrate which applied sensitization liquid was carried out for 10 minutes on the 80-degree C hot plate. Next, it placed so that a spreading side might turn to the hot plate which kept this sample (spreading glass substrate) at 50 degrees C up, and the weight of 2kg of loads was carried for the glass plate of the size same on that spreading side as the above superposition and on it, and it was left for 10 minutes. then, the adhesion of a resist coat and a glass plate, i.e., the force taken to remove the glass plate of two upper and lower sides, — evaluating — this — warming — it considered as the scale of the tuck free nature at the time, the above — warming — the following criteria estimated the tuck free engine performance at the time.

O : there is no tuck. (Even if it does not apply the force, it can exfoliate easily)

++ : There is a tuck a little. (It can exfoliate, if a little force is applied)

x : There is a tuck. (It cannot exfoliate, even if it applies the force considerably)

[0031] (2) The thickness before remaining-rate-of-membrane development and the thickness after development were measured with the weight method.

O : it had 90% or more of thickness before development.

++ : It had 85 – 90% of thickness before development.

x : It had only 85% of thickness before development.

[0032] (3) The sodium-carbonate water solution performed developing time development 25 degrees C of 1% of solution temperature, and time amount until it dissolves all the paint films for an unexposed part was made into developing time. In addition, in this invention, soluble means that this developing time is less than 2 minutes in a dilute-alkali water solution. The following criteria estimated development nature.

O less than [: 2 minute] — development possible **2- 5 minutes — development possible x : — the developing time exceeding 5 minutes — the need [0033] (4) Sensibility sensibility is Kodak Photographic Step Tablet It evaluated using No.2 and displayed by gray-scale sensibility, i.e., a number of stages. It is shown that it is high sensitivity, so that this number of stages is high.

(5) It measured using the resolving chart of a resolution negative and POJITAIPU. The line breadth 5, 10, 15, 20, 25, and 30 of a test pattern and 400–500-micrometer Rhine calculated the lower limit currently resolved clearly. It is shown that resolution is so good that this value is low.

[0034] (6) an adhesion profit **** resist paint film — JIS According to the D-020 examining method, the peeling trial (friction test) by the cellophane tape was performed, and generating of exfoliation was observed. The valuation basis is as follows.

O : adhesion is good. 100/100++ Adhesion and ***** 50/100–99/100x Adhesion ***** 0 / 100 – 49/100 [0035] (7) After carrying out etching-proof acidity-or-alkalinity ability postbake, the 45 degreeBe'ferric-chloride water solution of 50 degrees C of solution temperature performed spray etching for 5 minutes. Then, the pattern of a paint film was observed by the SEM photograph and viewing. Etching-proof acidity or alkalinity was performed by the following valuation basis.

O : — ++ : as which change is not regarded by the paint film — [0036] as which there is no x:glass whose gloss is lost in a paint film slightly, and pervasion is regarded by the paint film It sets in the example 2 example 1, and is SAIKUROMAP about a denaturation copolymer. It

replaced with the brand ACA200 and experimented by the same approach as an example 1.

* The physical-properties value acid number of ACA200 : 118 mg KOH/g double bond equivalent : 450 g/mol weight average molecular weight. The evaluation result obtained 15,000 was shown in Table 1.

[0037] It sets in the three to example 4 example 1, and is a bulking agent. The loadings of AEROSIL200 were replaced with 15g (example 3) and 35g (example 4), and it experimented by the same approach as an example 1. In addition, the loadings of AEROSIL200 were [as opposed to / in this case / said sensitization liquid undiluted solution 100 weight section] 0.58 and the 1.3 weight section, respectively. The obtained evaluation result was shown in Table 1.

[0038] In example 5 example 1, the photopolymerization nature vinyl monomer was replaced with cyclohexane dimethanol diacrylate, and it experimented by the same approach as an example 1. The obtained evaluation result was shown in Table 1.

[0039] It sets in the six to example 7 example 1, and is a bulking agent. Ultrafine particle-like silica powder was replaced with "AEROSIL130" (example 6) and "AEROSIL300" (example 7) from which the mean particle diameter made from Japanese Aerosil differs, and it experimented by the same approach as an example 1. The physical properties of each silica powder are as follows.

AEROSIL130 AEROSIL300 Specific surface area by – BET adsorption method m2/g 130 ** 25 300 ** 30 The pH value in –4% water dispersion 4.0–4.5 3.8–4.3 The pitch diameter of – primary particle nm Abbreviation 18 Abbreviation 7 – bulk specific gravity g/L Abbreviation 50 Abbreviation 50 –SiO2 Content % > 99.9 > 99.9 In addition, the loadings of AEROSIL200 are [as opposed to / in this case / said sensitization liquid undiluted solution 100 weight section] the 0.98 weight section. The obtained evaluation result was shown in Table 1.

[0040] It sets in the example of comparison 1 example 1, and is a bulking agent. It experimented by the same approach as an example 1 without completely blending AEROSIL200. The obtained evaluation result was shown in Table 1.

In example of comparison 2 example 1, the loadings of a bulking agent "AEROSIL200" were set to 4g, and it experimented by the same approach as an example 1. In addition, AEROSIL200 was [as opposed to / in this case / said sensitization liquid undiluted solution 100 weight section] the 0.16 weight section. The obtained evaluation result was shown in Table 1.

[0041] In example of comparison 3 example 1, the loadings of a bulking agent "AEROSIL200" were set to 60g, and it experimented by the same approach as an example 1. In addition, AEROSIL200 was [as opposed to / in this case / said sensitization liquid undiluted solution 100 weight section] the 2.2 weight sections. Consequently, the obtained sensitization liquid was with which a very high thixotropy is shown, and only an uneven paint film is obtained, but it is hard to present practical use.

[0042] In example of comparison 4 example 1, it replaced with the bulking agent "AEROSIL50", and experimented by the same approach as an example 1. The physical-properties value of the used silica powder is as follows.

– Specific surface area by the BET adsorption method m2/g 50**15 300 ** 30 – The pH value in 4% water dispersion 4.3–5.0 3.8–4.3 The pitch diameter of – primary particle nm Abbreviation 30 Abbreviation 7 – bulk specific gravity g/L Abbreviation 50 Abbreviation 50 –SiO2 Content % > 99.9 > 99.9 The loadings of AEROSIL50 are [as opposed to / in 99.9, in addition this case / said sensitization liquid undiluted solution 100 weight section] the 0.98 weight section. The obtained evaluation result was shown in Table 1.

[0043]

[Table 2]

http://www4.ipd.ncipi.go.jp/cgi-bin/tran_web.cgi_ejje

2006/12/01

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表 1 試験評価結果

試験評価項目	実証例							比較例			
	1	2	3	4	5	6	7	1	2	3	4
発振率	○	○	○	○	○	○	○	○	○	○	○
加速時のショックフリー性 (50℃加速)	○	○	○	○	○	○	○	×	△	評 価 不 能	△
現像性 (0.5X _{UV} , CO ₂ 水溶液)	○	○	○	○	○	○	○	○	○	○	○
グレイスケール感度 (2段階)	10	10	10	10	10	10	10	11	11		9
解像度 (μm)	10	10	10	10	10	10	10	10	10		9
密着性	○	○	○	○	○	○	○	○	○	△	△
耐エッチング酸性 (塩化第二水素水溶液)	○	○	○	○	○	○	○	○	○	○	△

[Translation done.]